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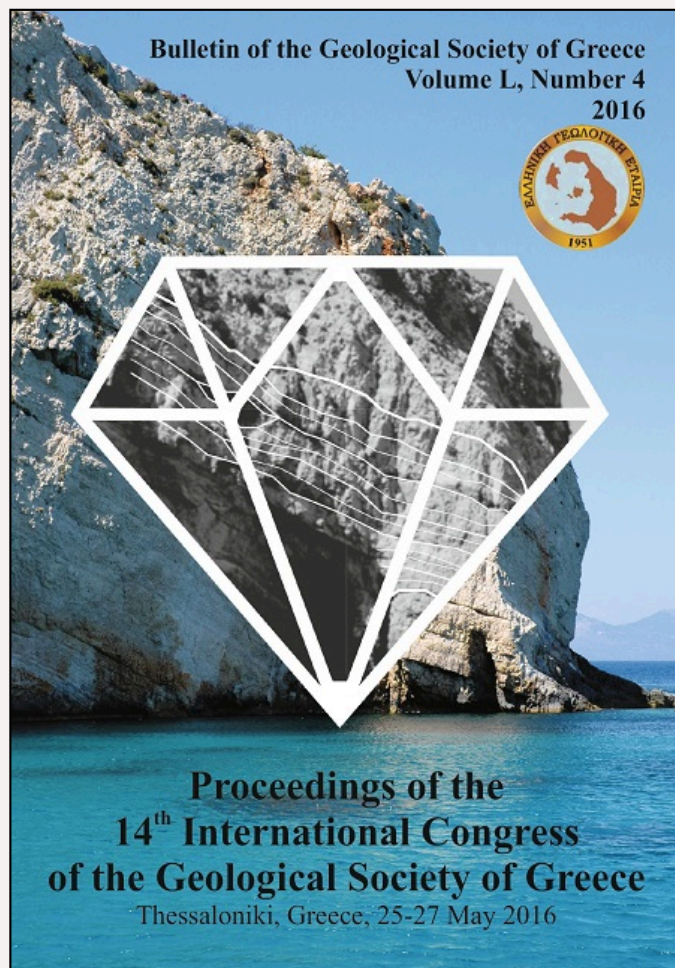
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MARIALITIC SCAPOLITE OCCURENCES FROM THE KIMMERIA-LEFKOPETRA METAMORPHIC CONTACT, XANTHI (N. GREECE)

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Abstract

Emplacement of the Xanthi Plutonic Complex within the Rhodope Massif of N. Greece created an extensive metamorphic aureole around the plutonite. The aureole contains two areas of intense scapolitization in the contacts between granodiorite and biotite-gneiss and between monzonite and sandstone, the latter cross-cut by andesite dykes. This paper reports the results of a mineralogical and geochemical study into the formation of the scapolites and particularly the nature of the plutonite-derived hydrothermal fluids from which scapolites were formed.

Keywords: Xanthi Plutonic Complex, scapolitization, marialite.

Περίληψη

Η διείσδυση του πλουτωνίτη της Ξάνθης στην μάζα της Ροδόπης στη Β. Ελλάδα δημιούργησε μια εκτεταμένη μεταμορφική άλω γύρω από τον πλουτωνίτη. Η άλω περιέχει δυο περιοχές έντονης σκαπολιθίωσης στις επαφές μεταξύ γρανοδιוריτί και βιοτιτικού γνεύσιου και μεταξύ μονζονίτη και ψαμμίτη στον οποίο διεισδύουν ανδεσιτικές φλέβες. Η παρούσα εργασία παρουσιάζει τα αποτελέσματα ορυκτολογικής και γεωχημικής έρευνας για το σχηματισμό των σκαπόλιθων και ιδιαίτερα για τη φύση των υδροθερμικών ρευστών προερχόμενων από τον πλουτωνίτη από τα οποία σχηματίστηκαν οι σκαπόλιθοι.

Λέξεις κλειδιά: Πλουτωνίτης της Ξάνθης, σκαπολιθίωση, μαριάλιθος.

1. Introduction

Scapolite-group minerals are tetragonal framework aluminosilicates with a general formula: $M_4T_{12}O_{24}A$, where $M = \text{Ca, Na, K and Sr}$, $T = \text{Si and Al}$ and $A = \text{Cl, CO}_3$, and SO_4 (Deer *et al.*, 2013). Their compositions vary between the end-members marialite ($\text{Na}_4(\text{Al}_3\text{Si}_9\text{O}_{24})\text{Cl}$) and meionite ($\text{Ca}_4(\text{Al}_6\text{Si}_6\text{O}_{24})\text{CO}_3$) which are not found in nature but can be synthesized (e.g. Eugster and Prostka, 1960; Eugster *et al.*, 1962; Goldsmith and Newton, 1977; Sokolova *et al.*, 1996; Sherrieff *et al.*, 2000). In natural systems, the composition of Cl-bearing scapolite ranges between three end-members: $\text{Na}_4(\text{Al}_3\text{Si}_9\text{O}_{24})\text{Cl}$, $\text{Na}_3\text{Ca}(\text{Al}_4\text{Si}_8\text{O}_{24})\text{Cl}$, and $\text{NaCa}_3(\text{Al}_5\text{Si}_7\text{O}_{24})\text{CO}_3$ (Pan, 1998). Scapolite has no industrial uses but is a minor gemstone that exhibits chatoyancy, creating a cat's eye effect when cut *en cabochon* (Bonewitz, 2005).

Scapolite is found in a wide range of geological settings but most commonly in metamorphic and metasomatic rocks. Its presence has been described in low-pressure skarns, low to medium pressure regional metamorphic rocks, medium to high pressure/depth assemblages of amphibolite and granulite facies and even in kimberlites and basalts (Baker and Newton, 1994 and references therein). It is also thought to occur as a primary mineral in alkaline igneous rocks (Larsen, 1981; Goff *et al.*, 1982). Well-known occurrences of scapolite in Greece include the Serifos Island skarn (Mposkos, 1978), the Kerdillion Unit amphibolites of the Serbo-Macedonian Massif (Rentina and Stratoni areas) (Kassoli-Fournaraki, 1981), the Chalkidiki peninsula quartz amphibolites (Sarti area) (Kassoli-Fournaraki, 1991) and the eastern Rhodope amphibolitized eclogites (Organi-Kimi area) (Mposkos and Mpaziotis, 2005).

Where scapolite occurs proximal to magmatic intrusions, its formation is likely to be due to metasomatic processes (Deer *et al.*, 2013). Scapolitization can occur sequentially or contemporaneously with other metasomatic processes like albitization, as both require saline fluids (Touret and Nijland, 2013). However, why scapolitization occurs instead of other metasomatic processes remains unclear. An obviously important control is the nature of the hydrothermal fluid from which it forms. To investigate this we have carried out a case study in the metamorphic aureole of the Xanthi Plutonic Complex (XPC), Rhodope Massif, Greece, where scapolite is particularly well developed and it has a clear spatial and temporal association with intrusive magmatic rocks (Christofides, 1977). The objective of this study was to carry out mineralogical and geochemical studies on scapolite to investigate the nature of metasomatic fluids responsible for its formation.

2. Geological Setting

The evolution of the Rhodope Massif during the Oligocene to Miocene was heavily influenced by the presence of fault-controlled sedimentary basins (Caracciolo *et al.*, 2011; Kiliass *et al.*, 2011) and calc-alkaline to high-K calc-alkaline intrusive and extrusive magmatism. Intrusive rocks include those of the XPC which were emplaced into gneisses, mica schists, amphibolites, calc-silicate rocks, marbles and Eocene-Oligocene sedimentary rocks of the Rhodope Massif (Fig. 1). To the south, the XPC has a fault contact with Neogene and Quaternary rocks (Christofides *et al.*, 2010). From geophysical data (Maltezou and Brooks, 1989; Tsokas *et al.*, 1996), the XPC is a laccolith-shaped body that extends several kilometers to the south.

The 40 km² (10.5 km length and 4.5 km width) XPC mainly consists of two rock groups: an 'acid' group containing granodiorites grading into monzogranites, with microgranular mafic enclaves of quartz diorite composition; and a 'basic' group composed of monzonite/quartz monzonite, quartz monzodiorite and subordinate monzogabbro and olivine gabbro. The SiO₂ content of the XPC ranges from 62-69 wt.% for the 'acid' group and 44-61 wt.% for the 'basic' group (Christofides *et al.*, 2010). The age of the XPC has been estimated at 25-29 Ma (Liati, 1986; Bigazzi *et al.*, 1994), however Christofides *et al.* (2012) recently determined an age of 34.3±0.5 Ma for the granodiorite rock type.

Christofides *et al.* (2010), estimated that the XPC initially crystallized under relatively dry conditions at 5.8 kbar pressure and 1300°C maximum temperature. This temperature reflects the initial crystallization of the gabbroic magma immediately after emplacement. In a subsequent phase, the water content of the melt increased (to more than 4 wt.%) at an average temperature of 870°C. The increase in melt-water content allowed magma to reach higher crustal levels at lower pressure (average of 1.8 kbar). The 'acid' group crystallized under oxidizing conditions at 729°C average temperature and 0.7 kbar pressure (Christofides *et al.*, 2010). These P/T conditions are significantly lower compared to those of the 'basic' group. This fact potentially suggests a different origin and/or evolution of the 'acid' and 'basic' group.

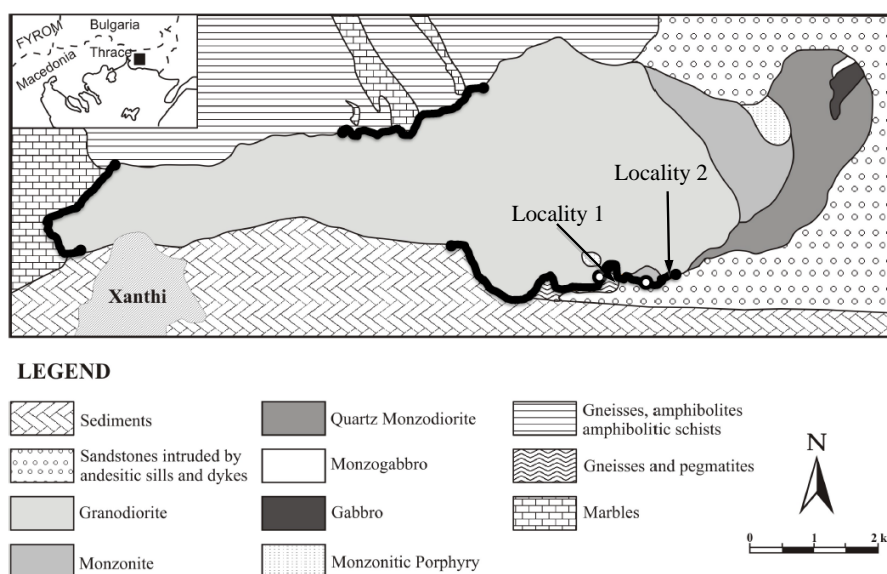


Figure 1 - Geological map of the Xanthi Plutonic Complex (modified after Christofides *et al.*, 2010). The contact metamorphic aureole surrounds the plutonite but is more intense and visible in the bold areas. The two points indicate the positions of the scapolite occurrences. Scapolite at Locality 1 occurs at the contact between granodiorite and biotite-gneiss whereas that at Locality 2 is at the contact between monzonite and sandstones (intruded by andesitic dykes).

The XPC, which is mostly undeformed and unweathered, has an extensive (around 300m thick) contact metamorphic aureole that is mostly visible in contact with marbles and contains a massive Au-bearing skarn-type mineralization, a Mo-Cu-Bi-W vein mineralization and a magnetite ore deposit (Christofides, 1977; Liati, 1986; Vavelidis *et al.*, 1990; Skarpelis and Liati, 1991; Voudouris *et al.*, 2010; Melfos and Voudouris, 2012). Scapolite mostly occurs in the southern part of the complex, best seen north of Lefkopetra village (Fig. 1), at the 'Kimmeria-Lefkopetra' contact, between the granodiorite and biotite-gneiss (Locality 1) and monzonite and sandstones (intruded by andesite dykes) (Locality 2).

3. Materials and Methods

Scapolite samples were analyzed using a Philips PW1820/00 X-ray diffractometer equipped with a PW1710/00 microprocessor (CuK α radiation, Ni filter, 35 kV and 25 mA) at the Department of Mineralogy-Petrology-Economic Geology, School of Geology, Aristotle University of Thessaloniki (AUTH). Samples were typically scanned at room temperature over angles of 3-63° 2 θ with a 1.2° 2 θ minimum scan velocity. The resulting patterns were interpreted using PC-APD (1994) software by matching peaks with those for minerals in the ICDDPDF database. Imaging in backscattered electron mode (BSE, for average atomic number contrast) and chemical analyses were performed on polished thin sections and resin blocks in a JEOL JSM-840A scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDS) at the Interdepartmental Laboratory of Electron Microscopy of AUTH. The analyses were undertaken at an accelerating voltage of 20 kV and a probe current of 0.4 mA.

4. Results

Scapolite showed very different crystal sizes at the two locations in Fig. 1, reaching up to 10 cm in length at Locality 1 but being microscopic at Locality 2. In both locations, scapolite in hand specimen ranged from white to grey or colorless. Powdered samples analyzed by XRD had a marialite composition (Fig. 2). Rock samples from Locality 1 were composed of actinolite-clinopyroxene-scapolite-white mica, whilst those from Locality 2 were consisted of plagioclase-scapolite-clinopyroxene-titanite (Fig. 3). Scapolite from both localities is colorless in PPL, with low relief and poor {100} to indistinct {110} cleavage. Crystals from Locality 1 are often poikilitic containing inclusions of clinopyroxene. Those from Locality 2 surround and often partially replace primary plagioclase (by scapolitization). Where still present, the plagioclase is cloudy in appearance, which, from SEM-EDS analysis, is due to the presence of fine-grained (from less than 100 μm to a few mm) alteration phases including scapolite, calcite, white mica and orthoclase (Fig. 4). From semi-quantitative SEM-EDS analysis of scapolite from Locality 1 and 2, it can be classified as marialite, containing approximately 11.5 and 8 wt.% NaCl, respectively.

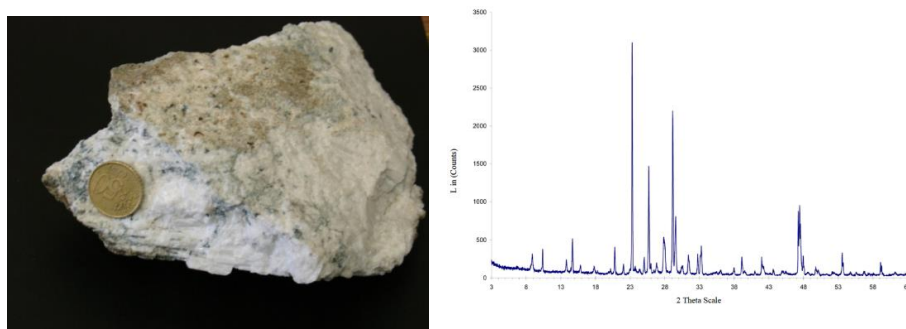
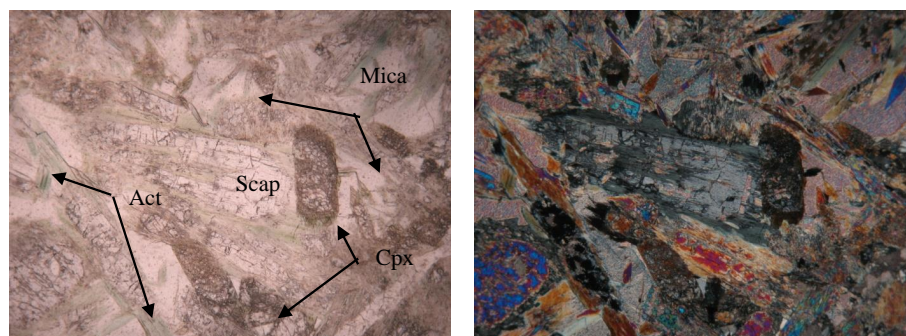


Figure 2 - Photograph of scapolite from Locality 1 (left) and its XRD pattern (right).



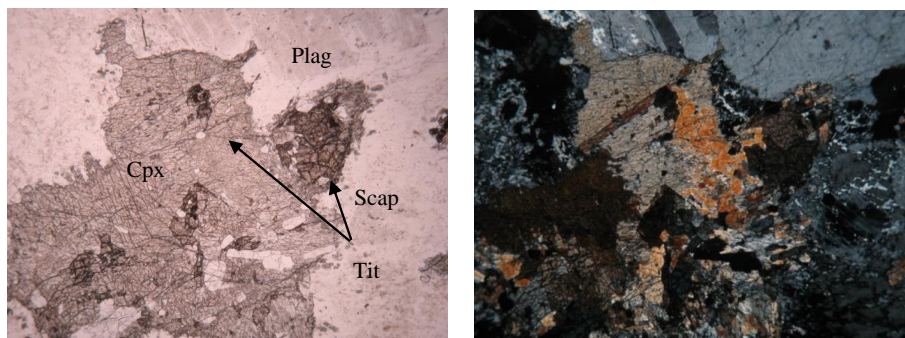


Figure 3 - Photomicrographs (40x) of scapolite from Locality 1 (upper) and 2 (lower) in plane- (PPL, left) and crossed-polarized light (XPL, right). Act = actinolite, Cpx = clinopyroxene, Mica = white mica, Plag = plagioclase, Scap = scapolite, and Tit = titanite.

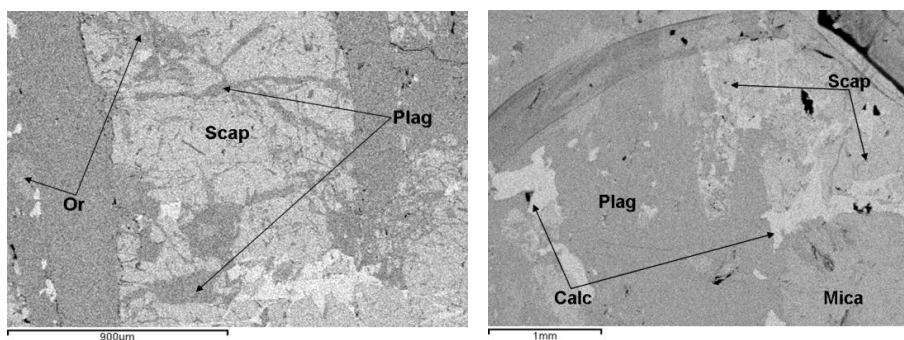


Figure 4 - BSE-SEM images of scapolite from Locality 2. Scap = scapolite, Plag = plagioclase, Calc = calcite, Mica = white mica and Or = orthoclase.

5. Discussion

Scapolite within skarns almost invariably shares its host's metasomatic origin, formed due to the action of metasomatic fluids expelled during the emplacement and crystallization of proximal magmatic intrusions (Einaudi *et al.*, 1981). In most circumstances, scapolite forms by replacement of plagioclase due to the process of scapolitization. Such replacement is thought to be driven by interaction of plagioclase with fluids containing Cl^- , CO_2 , SO_3 and Na^+ , rather than by isochemical transformation (Kullerud and Erambert, 1999). When the fluids contain high concentrations of SO_2 and CO_2 , the formation and stabilization of meionite (Ca-rich scapolite) is favoured. On the contrary, a Cl-rich fluid phase favours the formation and stabilization of marialite (Na-rich scapolite). The composition of scapolite is largely controlled by the following linked substitutions: $\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$, $\text{Al}^{3+} \leftrightarrow \text{Si}^{4+}$ and $\text{Cl}^- \leftrightarrow \text{CO}_3^{2-}$. All three substitutions are active in Na-rich scapolite [$\text{Ca}/(\text{Ca}+\text{Na}) < 0.75$], whereas Cl is completely replaced by CO_3 in Ca-rich scapolite [$\text{Ca}/(\text{Ca}+\text{Na}) > 0.75$] and hence the chemical reaction is controlled only by the $\text{NaSi} \leftrightarrow \text{CaAl}$ double substitution (Strauss, 2003).

Scapolite can be a potential indicator for the activity of volatiles during various processes that take place in the Earth's crust. This is because of its ability to incorporate volatile elements and compounds such as Cl, CO_2 and SO_3 , and due to the fact that scapolite can equilibrate in a wide range of pressure and temperature environments. There are many papers in the literature that contain

quantitative calculations on the volatile activity of metamorphic fluids based on the chemistry of scapolite (e.g. Ellis, 1978; Moecher and Essene, 1991; Harley *et al.*, 1994; Gómez-Pugnaire *et al.*, 1994). Nowadays, there are two diametrically opposed views on the distribution of volatile components between scapolite and fluids. The first one suggests that the Cl content of scapolite is heavily dependent on the limitations imposed by the cationic lattice in the balance of valences (Pan *et al.*, 1994). The second one claims that Cl content of scapolite is mainly controlled by the activity of NaCl in fluids that are in equilibrium with the mineral (Jiang *et al.*, 1994).

In addition to this, F and Cl are ubiquitous (in various amounts from ppm to wt.%) in fluids at all crustal levels (Markl and Piazzolo, 1998). These two elements occur in many metamorphic rock-forming minerals and consequently can be determined in order to estimate their ratios in metamorphic fluids (Munoz and Swenson, 1981; Zhu and Sverjensky, 1991; Harley and Buick, 1992; Markl and Bucher, 1998). As a result, the chemistry of scapolite, and particularly its Cl and CO₂ contents, in relation to the Cl and F content of other coexisting common metamorphic rock-forming minerals, such as amphibole, mica, apatite and titanite, can be used as tracers for the chemical composition of the metamorphic fluid (Ellis, 1978; Munoz and Swenson, 1981; Binder and Troll, 1989; Mora and Valley, 1989; Kullerud, 1996; Rebbert and Rice, 1997; Markl and Bucher, 1998; Kullerud and Erambert, 1999; Yardley *et al.*, 2000; Svensen *et al.*, 2001).

The formation of marialite requires saline (around 20 wt.% NaCl) metasomatic fluids (Vanko and Bishop, 1982), which means that Cl-rich scapolite is an indicator of high NaCl activity during crystallization (Orville, 1975; Ellis, 1978; Vanko and Bishop, 1982). NaCl may have been original to the system or may have been derived from an external source (such as nearby sedimentary rocks, halite-bearing rocks or brines) through fluid migration. Fluid inclusion studies indicate that the salinity of metamorphic fluids ranges from 0-6 wt.% in pelitic schists and gneisses, 20-25 wt.% in calcareous rocks and up to 50 wt.% NaCl equivalent in evaporates (Mora and Valley, 1989, and references therein). However, when scapolite contains low levels of NaCl (<20 wt.%), as in those from both localities, it is unclear if it is formed from low salinity magmatic fluids, ingress of saline meteoric waters or a mixture of both, which can cause a decrease in fluid temperature and salinity.

Finally, NaCl-rich scapolite was synthesized at temperatures higher than 700-800°C and at low to high pressure (Eugster and Prostka, 1960; Newton and Goldsmith, 1975). This temperature range is not significantly different from the crystallization temperature of granodiorite and monzonite. Hence, it can be considered that scapolite from Locality 1 formed at 729°C and 0.7 kbar, and in equilibrium with the fluid phase, as it seems that the plutonic plagioclase was completely replaced by scapolite. Incomplete scapolitization at Locality 2 took place at 870°C and approximately 1.8 kbar pressure. Scapolitization at both localities occurred under the influence of magmatic fluids emanating from crystallizing magma that formed the XPC, particularly after the initial stage of cooling when melt-water contents increased allowing the magma to reach shallower emplacement levels.

6. Conclusions

Scapolite in the case study was formed and developed by replacement of igneous plagioclase through metasomatic reactions within the contact aureole of the XPC. Complete scapolitization at Locality 1 took place at 729°C and 0.7 kbar by interaction of the cooling granodiorite with fluids containing 11.5 wt.% NaCl. On the other hand, incomplete scapolitization at Locality 2 occurred at slightly higher temperatures and pressures (870°C and 1.8 kbar) and during interaction with lower salinity (8 wt.% NaCl) fluids during the cooling of monzonite. Differences in the chemistry of scapolite from Locality 1 and 2, with varying substitution of $\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$, $\text{Al}^{3+} \leftrightarrow \text{Si}^{4+}$ and $\text{Cl}^- \leftrightarrow \text{CO}_3^{2-}$, are likely to reflect slight differences in the salinity of the metasomatic fluids from which they were formed. However, the cause of the variations in the temperature and salinity of the metasomatic fluids remains to be determined. Further to this, the reasons for the abrupt end to the scapolitization process

at Locality 2, as well as the role of the nearby sediments and andesitic intrusions as a potential source for NaCl-rich fluids, requires further research.

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